

OPIC
OFFICE DE LA PROPRIÉTÉ
INTELLECTUELLE DU CANADA



CIPO
CANADIAN INTELLECTUAL
PROPERTY OFFICE

Ottawa Hull K1A 0C9

(21) (A1) 2,129,463
(22) 1994/08/04
(43) 1995/02/13

(51) Int.Cl. ⁵ G01N-031/22; G01N-021/78; A61L-002/26

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Formaldehyde Detecting Paper

(72) Nakano, Nobuo - Japan ;

(71) Riken Keiki Co., Ltd. - Japan ;

(30) (JP) 220623/1993 1993/08/12
(JP) 41930/1994 1994/02/16

(57) 6 Claims

5,091,0/87

Notice: This application is as filed and may therefore contain an incomplete specification.



Industrie Canada Industry Canada

3488

Canada

BEST AVAILABLE COPY

2129463

SPECIFICATION

Title of the Invention

Formaldehyde Detecting Paper

Background of the Invention

This invention relates to formaldehyde detecting paper used for the detection of formaldehyde present in the atmosphere by using a coloring reaction.

Description of the Prior Art

A large space such as a sickroom is sterilized by filling the space with formaldehyde generated from a liquid prepared by dissolving formaldehyde in ethanol or a solid form of formaldehyde. As formaldehyde remains intact in the sterilized space, it is necessary to confirm that the concentration of residual formaldehyde is not higher than the level specified by environmental control standards.

Semiconductor gas sensors are often used for this kind of measurements. However, semiconductor gas sensors do not have sufficient sensitivities to measure the concentrations specified by environmental control standards (TLV 1 ppm). Besides, they have high sensitivities to other gases, such as ethanol used for preventing polymerization of formaldehyde and ammonia gas used for neutralizing the formaldehyde that remains after completion of sterilization. Therefore, semiconductor gas sensors do not have high enough reliability required in the measurement of

formaldehyde at such low concentrations as are specified by environmental control standards.

Many problem-solving methods so far proposed detect the presence of formaldehyde by utilizing colorations resulting from the reaction with, for example, silver ethylenediamine, nickel potassium cyanide, pararosaniline hydrochloride and acetylacetone, and in the AHMT process. Using reagents, however, these conventional methods require considerable manipulative skill in analytical work. On the other hand, introduction of automatic control in analysis is costly.

Summary of the Invention

To overcome these problems, the detecting paper of this invention comprises a carrying paper of porous substance covered with an acid salt of hydroxylamine and a hydrogen ion concentration indicator that changes its color in acidic environments and detects the presence of an acid resulting from the reaction of the acid salt of hydroxylamine with formaldehyde.

Object and Effect of the Invention

A first object of this invention is to provide formaldehyde detecting paper that detects the concentration of formaldehyde with high accuracy and reliability based on traces of reaction without using reagent and expensive equipment.

A second object of this invention is to provide formaldehyde detecting paper that detects extremely low concentrations of formaldehyde of the order of a few ppm's even in the environment with a relative humidity lower than the average.

The formaldehyde detecting paper of this invention detects and distinguishes formaldehyde from other gases present in the environment. This paper allows easy measurement of formaldehyde concentration while eliminating the need for using liquid reagents.

Furthermore, the formaldehyde detecting paper of this invention detects low concentrations of formaldehyde of the order of a few ppm's present in the environment with low relative humidities from traces of reaction formed on the porous carrier. In addition, the formaldehyde detecting paper of this invention permit long storage as exposure to such weakly acidic gases as carbon dioxide present in the environment does not cause discoloration.

Brief Description of the Drawings

Fig. 1 is a cross-sectional view of an example of a measuring device that uses the formaldehyde detecting paper of this invention. Fig. 2 plots the relative output characteristic of a first embodiment of the formaldehyde detecting paper of this invention. Fig. 3 plots the relative output characteristic of a second embodiment of the

formaldehyde detecting paper of this invention. Fig. 4 compares the relative output characteristic of a third embodiment of the formaldehyde detecting paper of this invention with that of a detecting paper covered with hydroxylamine phosphate and methyl red.

Description of the Preferred Embodiments

[Example 1]

A first solution was prepared by dissolving 1.0 gram of hydroxylamine sulfate in 100 milliliters of purified water. Then, a second solution was prepared by dissolving 0.02 gram of Metanil Yellow, a hydrogen ion concentration indicator that changes its color when reacted with sulfuric acid, and 15 milliliter of glycerin in methanol of the amount that makes the total quantity of the solution 100 milliliter.

A coloring liquid was prepared by mixing the first and second solutions. The carrier, such as filter paper of cellulose, was impregnated with the obtained coloring liquid. After the excess coloring liquid has been squeezed out by rubber rollers or other similar means, the organic solvent was air-dried at approximately 40° C.

Then, a detecting paper of porous substance covered with 0.35 gram of hydroxylamine sulfate, 0.15 gram of Metanil Yellow and 21 grams of glycerin per square meter was obtained.

Fig. 1 shows an example of an instrument that determines the concentration of formaldehyde by using the gas detecting paper of this invention. In the drawing, reference numeral 1 designates a gas suction device provided in the path of a tape of detector tape 2. The gas suction device 1 has a through hole 3 having a diameter of approximately 1 cm that opens in the surface thereof that faces the detecting paper 2. A negative pressure is supplied from a suction pump, not shown, through a pipe 4.

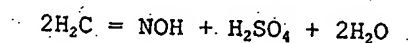
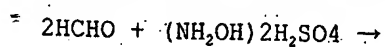
Reference numeral 5 denotes a measuring head disposed on the other side of the detecting paper 2 opposite to the through hole 3 in the gas suction device 1. The measuring head 5 constitutes a light-shielding means having a gas inlet 6 located in a position opposite to the through hole 3 in the gas suction device 1. The measuring head 5 contains a light-emitting diode 7 emitting a light having a peak wavelength of 555 nm and a pin-type photodiode 8 that exhibits maximum sensitivity to a light having a wavelength of 560 nm. The light-emitting diode 7 and photodiode 8 are disposed in such a position that they can detect a trace of reaction formed on the detecting paper 2.

After the tape of gas detecting paper 2 is set over reels 10 and 11, the suction pressure supplied from the pump not shown draws the object gas through an intake 9 to the measuring head 5. The object gas from the gas inlet 6

2129463

is discharged outside through the pipe 4 after passing through the tape of detecting paper 2 and the through hole 3. When the object gas passes through the tape of detecting paper 2, the water retained by the glycerin on the tape 2 absorbs formaldehyde therefrom.

The absorbed formaldehyde reacts with hydroxylamine sulfate present on the detecting paper 2 to produce sulfuric acid as a result of the following reaction:



The produced sulfuric acid reacts with Metanil Yellow that then changes its color according to the concentration of formaldehyde.

After an exposure time of a given length, such as approximately 40 seconds, has passed, the suction of the object gas is stopped to determine the optical concentration of the trace of reaction. The light from the light-emitting diode 7 is absorbed according to the optical concentration of the trace of reaction formed on the surface of the detecting paper 2. Therefore, the concentration of the formaldehyde that has passed through the tape can be obtained by determining the difference in optical concentration between the optical concentration before the start of the measurement, or the background concentration of the tape, and the trace of reaction formed.

thereon. When the measurement of one specimen is complete, the takeup reel 10 is turned to feed an unused portion of the tape 2 into the measuring zone.

With the detecting paper set on the measuring instrument just described and the exposure time at 40 seconds, optical concentrations of traces of reaction were measured by varying the concentration of formaldehyde through 1000 ppm, 2000 ppm and so on. Detection with high reproducibility was possible up to approximately 3000 ppm, as indicated by solid circles (●) in Fig. 2.

When the exposure time was increased to 60 seconds, the relative detection output for the same formaldehyde concentration increased accordingly, as indicated by open circles (○).

The carrier used in the example described above was impregnated with glycerin. When the formaldehyde concentration was above 1000 ppm, the detecting paper exhibited substantially the same sensitivity whether glycerin was present or not. Thus, glycerin proved to be an effective additive for the detection of lower concentrations of formaldehyde.

The substance that produces acid by reaction with formaldehyde in the example just described was hydroxylamine sulfate. Hydroxylamine hydrochloride is another salt that hydroxylamine forms with a strong acid. When decom-

posed by formaldehyde, hydroxylamine hydrochloride produces an acid that forms a trace of reaction with Metanil Yellow that is a hydrogen ion concentration indicator. The detecting paper prepared with the use of hydroxylamine hydrochloride proved to provide substantially the same relative detection output as hydroxylamine sulfate.

In addition to Metanil Yellow, alizarin yellow, benzyl yellow and methyl yellow are also hydrogen ion concentration indicators that color when reacted with the acid formed by the reaction between formaldehyde and a salt formed by a strong acid and hydroxylamine.

The detection paper prepared by the same method using, in place of Metanil Yellow, alizarin yellow, benzyl yellow and methyl yellow also proved to be capable of detecting formaldehyde.

Being a hydrogen ion concentration indicator that changes its color when the concentration of hydrogen ion is within the range of pH 1.2 to pH 2.3, Metanil Yellow does not react at all with such weakly acidic gases as carbon dioxide and hydrogen fluoride present in the air, alkaline gases such as ammonia, and organic solvents such as alcohol. This feature permits not only detecting formaldehyde with high selectivity but also long storage without discoloration.

The example described above was the case of determin-

ing the presence of formaldehyde of such high concentration as of the order emitted from sterilizers or other similar devices. The detecting paper of this invention is also applicable to the formaldehyde of as low a concentration as only a few ppm's by extending the length of exposure time to approximately 3 minutes.

[Example 2]

A first solution was prepared by dissolving 1.0 gram of hydroxylamine phosphate in 100 milliliters of purified water. Then, a second solution was prepared by dissolving 0.04 gram of methyl red, a hydrogen ion concentration indicator that changes its color when exposed to a weak acid, and 15 milliliter of glycerin in methanol of the amount that makes the total quantity of the solution 100 milliliter.

To a coloring liquid prepared by mixing the first and second solutions was added a given amount, such as approximately 30 V/V %, of one of buffers to prevent the change of color by carbon dioxide in the atmosphere which consist of a combination of NaCO_3 and NaHCO_3 , Na_2CO_3 and NaOH , and NaHCO_3 and NaOH .

The carrier of such material as cellulose, was impregnated with the obtained coloring liquid. After the excess coloring liquid has been squeezed out by rubber rollers or other similar means, the carrier was air-dried

at approximately 40° C. The amount of the buffer must be such as is enough to allow it to perform its buffering function to the carbon dioxide in the atmosphere. If the buffer is insufficient, the hydrogen ion concentration indicator is colored by such weakly acid gas as carbon dioxide in the air. By contrast, a coloring liquid containing too much buffer contains so watery that its drying process becomes time-consuming and inefficient. Therefore, an optimum amount of buffer should preferably be added.

Then, a detecting paper of porous substance covered with 0.03 gram of hydroxylamine phosphate, 0.05 gram of methyl red and 21.5 grams of glycerin per square meter was obtained.

Fig. 3 shows the measurements obtained by exposing the detecting paper thus obtained and set on the measuring instrument described before for a period of three minutes to sample gases containing 0.2, 1.0 and 4.0 ppm of formaldehyde.

Obviously, the formaldehyde detecting paper prepared with the use of a hydrogen ion concentration indicator, such as the methyl red used in the example described above, that changes its color in the presence of a salt of hydroxylamine and a weak acid and sulfuric acid resulting from the decomposition thereof has high enough sensitivity to detect the presence of formaldehyde of such low concentra-

tions as not more than one-third of 1 ppm, which is the acceptable environmental limit (TLV), with a high degree of reliability. Therefore, the formaldehyde detecting paper thus obtained is suited for use in the monitoring of the concentration of formaldehyde in the environment.

Another detecting paper prepared with the use of the same quantities of the same constituents but hydroxylamine phosphate, which was replaced with hydroxylamine oxalate, also provided similar relative detection outputs.

In addition to methyl red, lacmoid and neutral red also serve as hydrogen ion concentration indicators coloring in the presence of phosphoric and oxalic acids. Detecting papers prepared by using in place of methyl red, also provided similar detection outputs.

The concentrations and quantities of the reagents used in the examples described above were selected to provide high stabilities and sensitivities and keep the change of the original color of the tape by the hydrogen ion concentration indicator to a minimum. Of course, similar effects are obtainable even if their concentration and quantity are increased or decreased within appropriate limits.

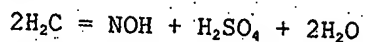
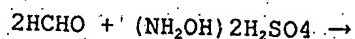
[Example 3]

In 30 milliliters of pure water was dissolved 1.0 gram of hydroxylamine sulfate. After adding 0.02 gram of methyl yellow, a hydrogen ion concentration indicator that changes

its color in the presence of sulfuric acid, and 5 milliliters of glycerin, an organic solvent, such as methanol or ethanol, was added to make the total quantity of the obtained liquid 100 milliliter. The carrier of porous substance, such as cellulose, was impregnated with the obtained coloring liquid. After the excess coloring liquid has been squeezed out by rubber rollers or other similar means, the organic solvent was air-dried at approximately 40° C.

Then, a detecting paper of porous substance covered with 1.3 gram of hydroxylamine sulfate, 0.026 gram of methyl yellow and 8 grams of glycerin per square meter was obtained.

When the detecting paper 2 was set on the measuring instrument described earlier for detection of formaldehyde in a sample gas, the paper absorbs formaldehyde when the sample gas passes therethrough. Then, as much sulfuric acid as is proportional to the concentration of formaldehyde was produced by the following reaction between the hydroxylamine sulfate on the detecting paper 2 and formaldehyde:



The methyl yellow on the detecting paper, which changes its color when the pH is between 2.9 and 4.0,

colored when exposed to a slight amount of sulfuric acid resulting from the reaction with formaldehyde, thereby leaving a trace of reaction of optical concentration corresponding to the concentration of formaldehyde.

With the detecting paper set on the measuring instrument described before and the exposure time at 5 minutes, optical concentrations of traces of reaction were measured by varying the concentration of formaldehyde in an atmosphere with as low a relative humidity as 30 % through 1, 2, 3 and 4 ppm. Then, relative detection outputs between 0.3 and 4 ppm were obtained, as indicated by solid circles (●) in Fig. 4.

The detection paper just described thus proved to be suited for the detection of formaldehyde at low concentrations in atmospheres with low humidities.

For comparison, measurements were made in the same atmosphere with a relative humidity of 30 % using a detection paper prepared by the use of hydroxyamine phosphate as the reagent that produces an acid as a result of a reaction with formaldehyde and methyl red as a hydrogen ion concentration indicator. The relative detection outputs obtained were only approximately one-tenth those of the detecting paper according to this invention, as indicated by open circles (○) in the same figure.

Thus, the detection paper just described proved to

have a high sensitivity to formaldehyde at low concentrations in atmospheres with particularly low relative humidities.

Being a hydrogen ion concentration indicator that changes its color within the pH range of 2.9 to 4.0, methyl yellow does not react at all with such weakly acidic gases as carbon dioxide and hydrogen fluoride present in the air and alcohol and other organic solvents used as the solvent for formaldehyde. Having adequate durability in the presence of hydrogen ions freed from the hydroxylamine sulfate on the tape while it is not in use, the tape remains as sensitive as it was immediately after production even after long storage.

The tape just described was prepared by the use of methyl yellow as a hydrogen ion concentration indicator. Methyl orange (coloring within the pH range of 3.1 to 4.4), benzyl orange (coloring within the pH range of 1.9 to 3.3) and tropeolin (coloring within the pH range of 1.4 and 3.2), which all change their color within the pH ranges similar to the range for methyl yellow, also proved to provide similar relative detection outputs and have as long shelf life as methyl yellow.

The concentrations and quantities of the reagents used in the examples described above were selected to provide high stabilities and sensitivities and keep the

2129463

change of the original color of the tape by the hydrogen ion concentration indicator to a minimum. Of course, similar effects are obtainable even if their concentration and quantity are increased or decreased within appropriate limits.

Claims

What is claimed is:

- (1) Formaldehyde detecting paper prepared by applying an acid salt of hydroxylamine and a hydrogen ion concentration indicator whose color changes in acidic atmospheres over a carrier of porous substance.
- (2) Formaldehyde detecting paper according to claim 1, in which the acid salt is hydroxylamine sulfate and the hydrogen ion concentration indicator is selected from the group of Metanil Yellow, alizarin yellow, benzyl yellow and methyl yellow.
- (3) Formaldehyde detecting paper according to claim 1, in which the acid salt is at least one selected from the group of hydroxylamine phosphate and hydroxylamine oxalate and the hydrogen ion concentration indicator is one selected from the group of methyl red, lacmoid and neutral red, and a buffering constituent is added thereto.
- (4) Formaldehyde detecting paper according to claim 3, in which the buffering constituent is at least one selected from the group of NaCO_3 and NaHCO_3 , Na_2CO_3 and NaOH , and NaHCO_3 and NaOH .
- (5) Formaldehyde detecting paper according to claims 1 to 3, in which the porous carrier contains a polyalcohol.
- (6) Formaldehyde detecting paper prepared by applying hydroxylamine sulfate and a hydrogen ion concentration

indicator selected from the group of methyl yellow, methyl orange, benzyl orange and tropeolin over a carrier of porous substance.

Abstract

Detecting paper for detecting the formaldehyde present in the atmosphere is prepared by applying hydroxylamine sulfate and Metanil Yellow that changes its color when exposed to sulfuric acid over a carrier of porous substance. When the sample gas passes through the porous carrier, the formaldehyde contained in it produces sulfuric acid (H_2SO_4) by decomposing the hydroxylamine sulfate as a result of the following reaction: $2\text{HCHO} + (\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{C} = \text{NOH} + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$. The sulfuric acid reacts with the Metanil Yellow on the porous carrier, thus leaving a trace of reaction proportional to the concentration of formaldehyde.

FIG. 1

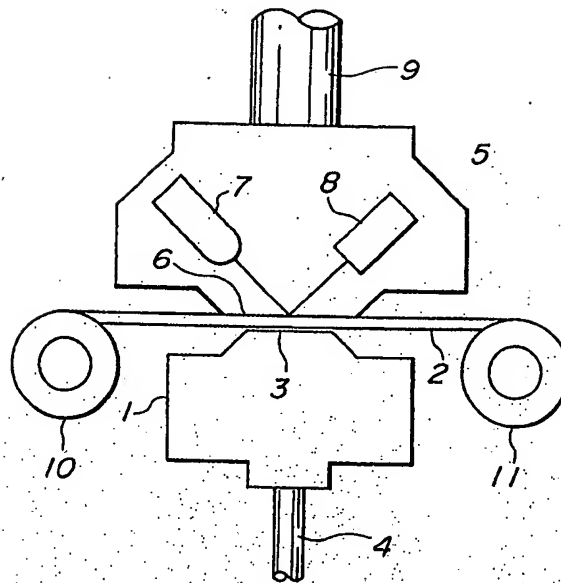


FIG.2

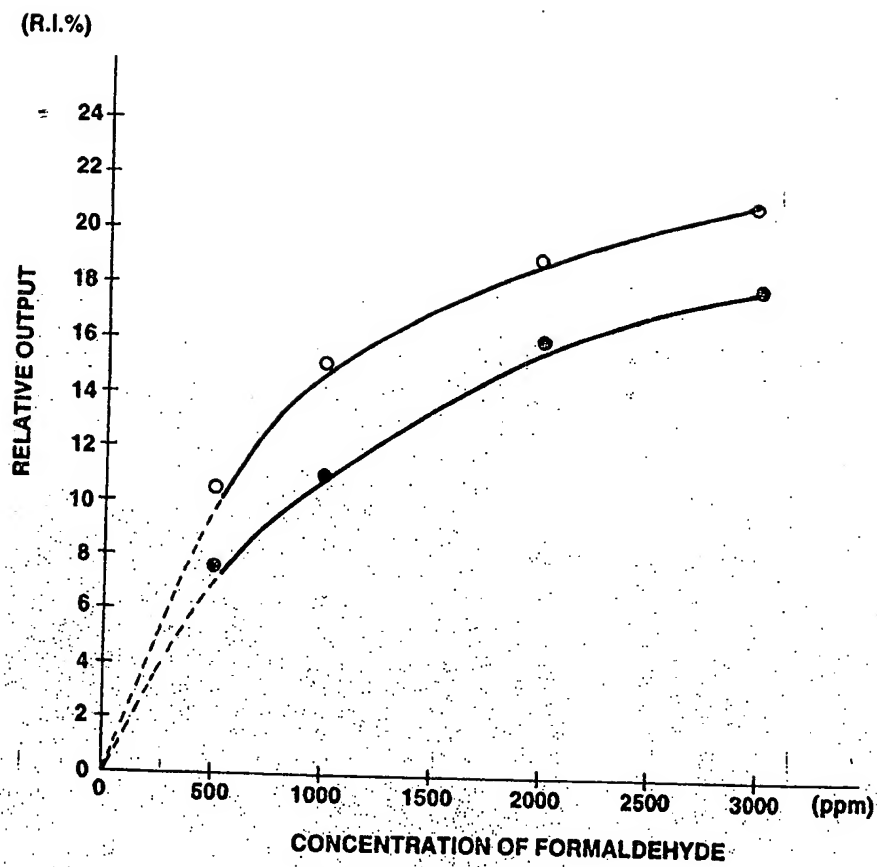


FIG.3

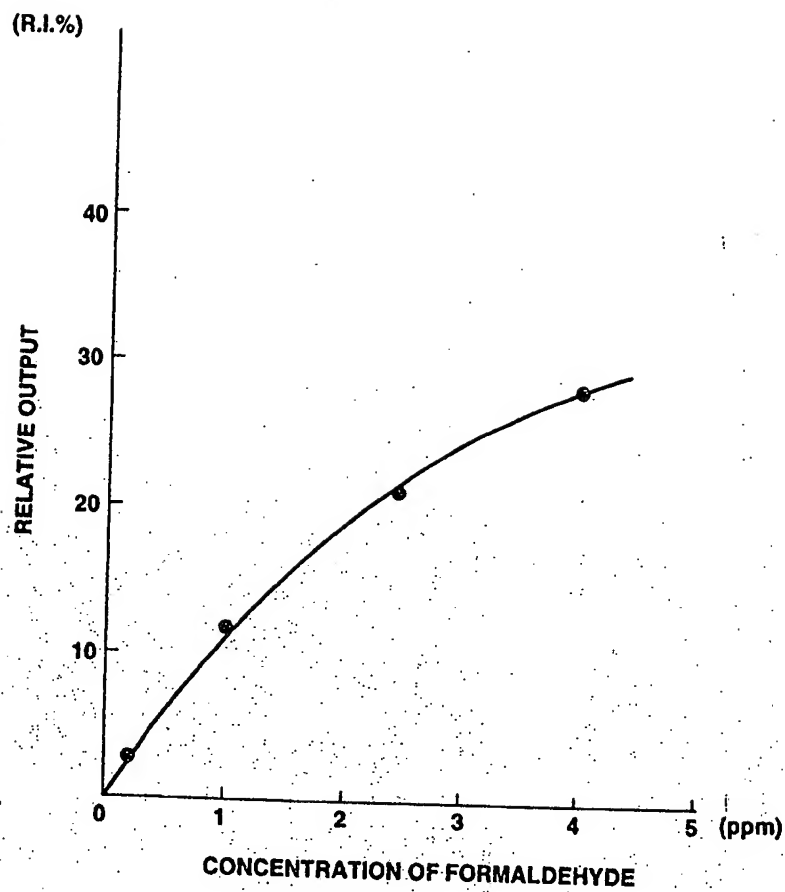
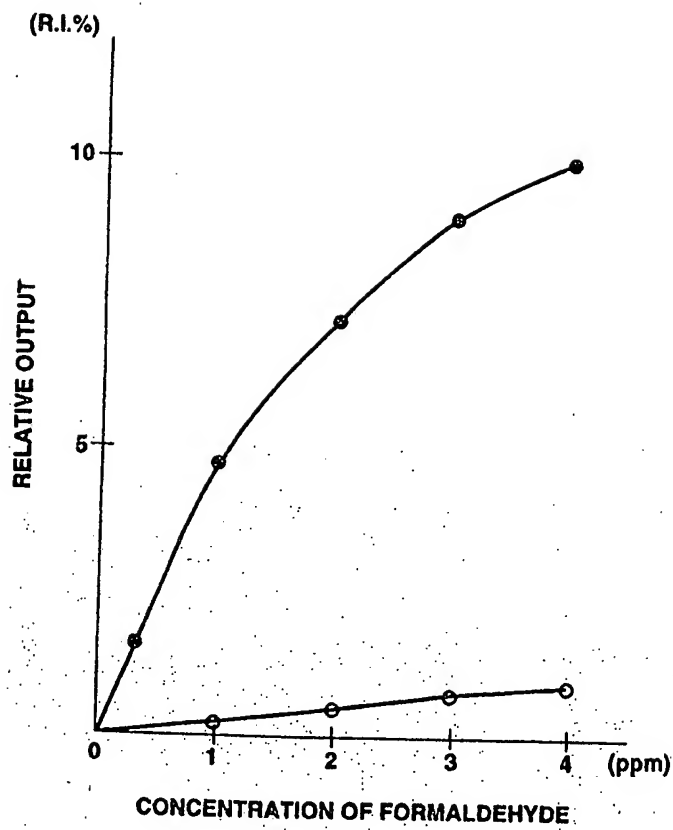


FIG.4

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.